The dissociation constant, on addition of ammonia, may increase, decrease or remain unchanged. Thus, for lithium picrate, there is an increase, for sodium iodide and silver nitrate, a decrease, while for sodium picrate there is no change. It appears that although free ions of lithium, sodium and silver become effectively smaller due to the presence of ammonia, in their ion pairs they may become either larger or smaller or undergo no change. Ion conductances are shown as a function of ammonia concentration in Fig. 3.

**2. Sodium Picrate in Presence of Water.**—In Table IV are given values for the constants of sodium picrate in the presence of water. Graphs are shown in Fig. 4.

As may be seen from Table IV, the conductance of the sodium ion in pyridine is increased on addition of water, but much less than on addition of ammonia. The increase is only 9% with 0.32 molar water. On the other hand, there is a marked increase of the dissociation constant, approximately six times for 0.32 molar water. This increase may be due, in part, to the higher dielectric constant of the water mixtures. At the concentration mentioned above, the dielectric constant is 7% greater than that of pyridine.

## V. Summary

1. The conductance of lithium and sodium picrates and of sodium iodide and silver nitrate have been measured in pyridine solutions to which ammonia had been added.
2. The conductance of sodium picrate has been similarly measured in pyridine to which water had been added.
3. Values of the limiting conductance and the dissociation constant have been derived for the salts in these solutions by the Fuoss method and ion conductances have been determined.
4. The conductance of the three cations increases markedly on addition of ammonia. At an ammonia concentration of 0.2 molar, the conductance increase for the lithium, sodium and silver ions is, respectively, 33, 42 and 15%.
5. The conductance increase for the sodium ion on addition of 0.2 molar water is 4.5%.
6. On addition of ammonia, the dissociation constant of lithium picrate increases somewhat. Those of sodium iodide and silver nitrate decrease and that of sodium picrate remains unchanged. The dissociation constant of sodium picrate is increased markedly on addition of water.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# The Effect of Centrifugal Force on Galvanic Potentials: (a) The Transference Numbers of Potassium Iodide, (b) The Iodide–Iodine Ion

BY D. A. MACINNES AND B. ROGER RAY[1a]

The effect of gradients of centrifugal force on the potentials of simple galvanic cells has been studied by Des Coudres[1] and more extensively by Tolman,[2] and some preliminary measurements have been reported by MacInnes.[3] Tolman and MacInnes used galvanic cells of the type

$$\underset{r_2}{(\mathrm{Pt})};\ \mathrm{I_2,\ KI,\ I_2};\ \underset{r_1}{(\mathrm{Pt})} \qquad \text{(A)}$$

in which two, otherwise identical, iodide–iodine electrodes with a uniform solution between them are placed at radii $r_1$ and $r_2$ in a centrifugal field. These researches have been interpreted by the equation

$$EF = 2\pi^2 n^2 (r_2^2 - r_1^2)[t_{\mathrm{K}}(M_{\mathrm{KI}} - \bar{V}_{\mathrm{KI}}\rho) - (M_{\mathrm{I}} - \bar{V}_{\mathrm{I}}\rho)] \qquad (1)$$

in which $F$ is the faraday, $n$ is the number of revolutions per second, $t_{\mathrm{K}}$ is the transference number of the cation constituent, $\rho$ is the density of the solution, $M_{\mathrm{KI}}$ and $\bar{V}_{\mathrm{KI}}$ are the molecular weights and partial molal volumes of potassium iodide, and $M_{\mathrm{I}}$ and $\bar{V}_{\mathrm{I}}$ are the atomic weight and partial atomic volume of iodine. It will be shown below that this is a limiting form of an equation which is based on more complete knowledge of the mechanism of cell A.

Studies of the closely related effect of differences of height on the potentials of galvanic cells have been made by Des Coudres[4] and more recently by Grinnell and Koenig.[5]

The results to be described below are the outcome of a long research undertaken to develop the centrifugal e. m. f. procedure into a precision method for obtaining transference numbers. It is of particular importance in that it can be used, as has been demonstrated by experiments already made, in the determination of transference numbers in non-aqueous solvents, where, due to Joule heat, the Hittorf and moving boundary methods encounter difficulties.

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(1a) National Research Council Fellow, 1945–1947, Merck Fellow in the National Sciences under the National Research Council, 1947–1948. Present address: Chemistry Department, University of Illinois, Urbana, Illinois.

(1) Des Coudres, *Ann. Physik*, **49**, 234 (1893).

(2) Tolman, *Proc. Am. Acad. Arts Sci.*, **46**, 109 (1910); THIS JOURNAL, **33**, 121 (1911).

(3) MacInnes, *Ann. New York Acad. Sci.*, **43**, 243 (1942).

(4) Des Coudres, *Ann. Physik*, **57**, 232 (1896).

(5) Grinnell and Koenig, THIS JOURNAL, **64**, 682 (1942).

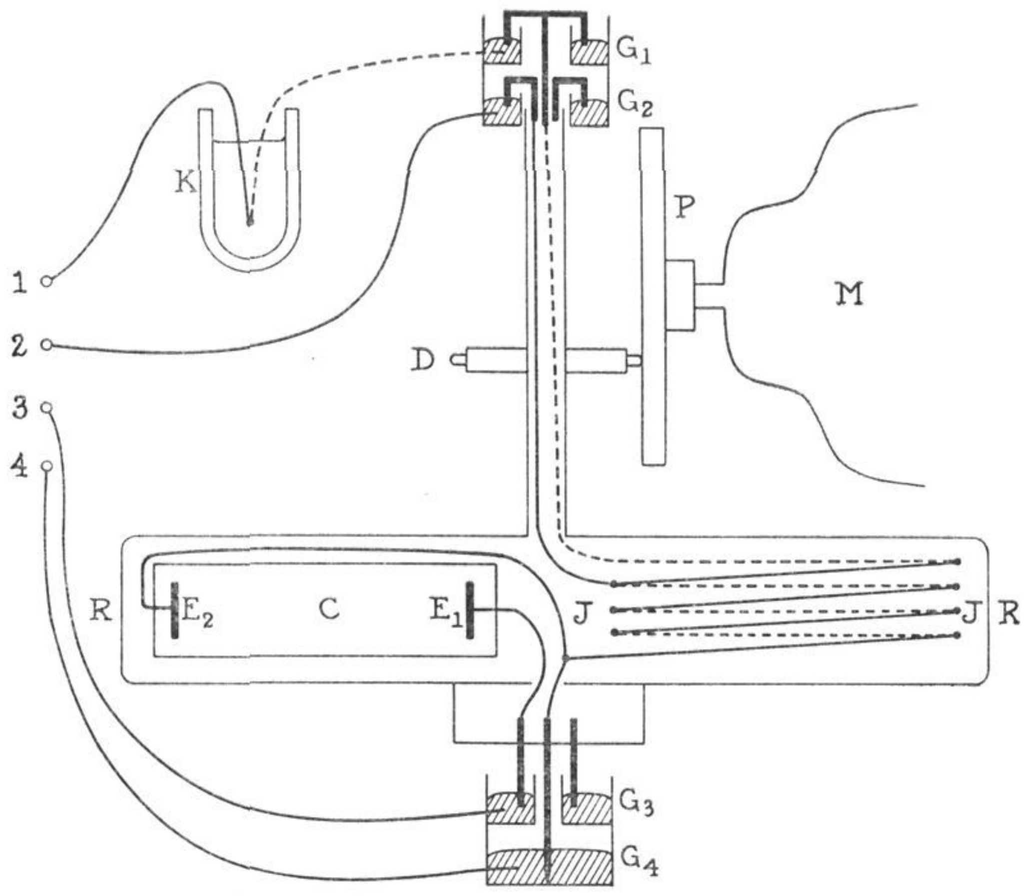

Fig. 1.—Diagram of apparatus.

## The Apparatus

The apparatus,[6] and the electrical connections, are shown diagrammatically in Fig. 1. The rotor R-R, which is a disk of magnesium 23 cm. in diameter and 5 cm. thick, is turned in a horizontal plane by means of the pressure of the disk D on the plate P, which is rotated by the synchronous motor M. The rotor speed can be varied by changing the position of the disk D with the relation to the plate P. The potential between the electrodes $E_1$ and $E_2$ of the galvanic cell C can be measured, during the rotation, by electrical contacts through the mercury commutators $G_3$ and $G_4$. The difference of temperature at radii corresponding to the positions of $E_1$ and $E_2$ is obtained by means of the thermojunctions J-J. Twenty-two junctions are used, and are actually arranged around cell C. The resulting thermopotential is measured between the commutators $G_2$ and $G_4$. Finally, the temperature of the rotor is found using a single junction in the rotor, the commutators $G_1$ and $G_2$ and the reference junction in the external ice-bath K. Thus by shifting the leads of the potentiometer to the appropriate pairs of the contacts 1, 2, 3 and 4 the e. m. f. of the cell, the differential temperature, and the temperature of the rotor may be measured. The temperature measurements are essential since the measured potentials have been found to be considerably affected by radial temperature gradients. Such gradients are minimized by surrounding the rotor with a chamber in which a vacuum of 1 $\mu$ or better can be maintained. This prevents the production of appreciable heat through gas friction. The heat generated at the vacuum bearing is controlled by the circulation of cooling water. Radial temperature differences are reduced to less than 0.01° by empirically choosing the temperature of the water. This arrangement also greatly reduces the rise, during a determination, of the temperature of the rotor.

The cell used in obtaining the data to be described below is shown in Fig. 2. The electrodes $E_1$ and $E_2$, which are platinum disks 1 cm. in diameter and 6.4 cm. apart, are sealed into the Jena 16 III glass ends of the cell. The platinum leads, $L_1$ and $L_2$, are enclosed in flexible plastic tubing. Filling and removal of the solution are carried out through the tube T which is closed with a ground-glass cap G. The cell is enclosed in the brass shell S, the space between the shell and the cell being filled with vaseline. This semi-fluid material helps to equalize the pressure on the two sides and bottom of the cell when in a centrifugal field. The Bakelite spacers, $V_1$ and $V_2$, hold the glass cell in a fixed position in the shell S.

To determine the radii $r_1$ and $r_2$ of eq. 1 the procedure was as follows. The glass portion of the cell shown in Fig. 2 was filled with, and immersed in, a microscope immersion oil with the same coefficient as glass, and the distances of the electrodes $E_1$ and $E_2$ from the top edge of the cell, P, which was ground flat, were read with an accurate comparator, equipped with a travelling microscope. The cell was then assembled, as shown in the figure, inserted in the centrifuge, and run at top speed to ensure definite settling into place. The cell assembly was then placed on a surface plate and the distance between the top edge P and the bottom of the brass shell S was measured with a depth gage. When placed in the rotor R-R of Fig. 1, the cell and its counterpoise rest against disks closing the ends of the channel. The effective diameter of the rotor, *i. e.*, the distance between these disks, was measured with the aid of a precision vernier caliper. With these data

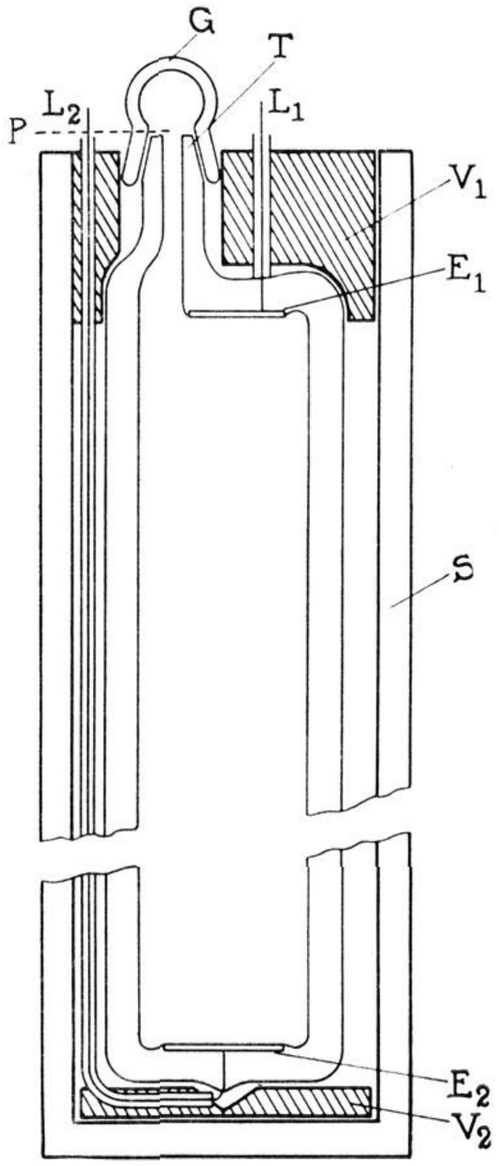

Fig. 2.—The galvanic cell.

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[6] The apparatus is more fully described in an article by Ray and MacInnes in the *Rev. Sci. Inst.*, **20**, 52 (1949).

the radii $r_1$ and $r_2$ may be computed. Since the electrodes $E_1$ and $E_2$ are not exactly parallel the factor $(r_2^2 - r_1^2)$, which for the cell used in these experiments was 86.04 cm.,$^2$ may be in error by about ±0.2%. Another design of cell which allows for greater precision in this factor has also been used in our work.[6]

It is quite important that the counterpoise have the same moment of inertia as the cell, *i. e.*, imitate it closely in distribution of weight, since otherwise the rotor may precess, and may not rotate about its geometrical center.

The mercury commutators $G_1$, $G_2$, $G_3$ and $G_4$ are described in detail elsewhere.[6] With them it was possible to make measurements to one microvolt, or better, of potentials developed in the rotor, this precision being necessary because the highest potentials determined are of the order of one millivolt.

The measurements of the speeds of rotation, which ranged between 400 and 7200 r. p. m., were made with the aid of stroboscopic patterns, as described in a paper from this Laboratory.[7] The rotating top surface of the commutator $G_1$ of Fig. 1 is painted black, with a white radial streak. This surface is illuminated by a stroboscopic lamp, which is operated from the local a. c. current, and yields flashes at the rate of 60 per second. At definite speeds stationary stroboscopic patterns are observed which are related by the formula r. p. m. = $(3600 \times m)/n$ in which $n$ is the number of bands in the pattern, and $m$ is the "multiplicity." Patterns are observed for integral values of $m$ and $n$ except when they have a common factor. As the same pattern occurs at a series of related speeds it is necessary to have a rough preliminary estimate of its value. This is furnished by a scale attached to the adjustment mechanism of the disk D of Fig. 1. Since stationary patterns could be obtained for indefinite periods, with occasional slight manual adjustments, the accuracy of the speed measurement was nearly that of the a. c. source, and was more than necessary for our purpose.

### The Preparation of the Solutions

The measurements described in this paper were made with 0.1941 *N* potassium iodide, to which varying amounts of iodine were added. In preparing this solution the best commercial salt was recrystallized several times, dried in an electric oven, followed by heating to 500° in a platinum boat in a current of purified nitrogen. The material was then weighed with the aid of the Richards bottling apparatus[8] procedure, after which the salt was dissolved in a weighed amount of conductivity water. A solution 0.1941 *N* in potassium iodide and 0.1585 *N* in iodine was made by adding a weighed amount of iodine (several times resublimed) to the stock potassium iodide solution. The solutions with smaller proportions of iodine were made by diluting, by volume, with carefully calibrated pipets, with the stock potassium iodide solution.

After many experiments designed to discover the source of persistent irregularities in the measurements, a source of difficulty was located in the minute suspended particles in the solutions. These were present although every effort had been made to ensure cleanliness in preparing the solutions. Such particles are far more important in this centrifugal work than in other e. m. f. measurements, since particles that are denser than the solution in which they are suspended will drift toward the outer, and less dense ones to the inner electrode, in both cases producing contamination of the platinum surface, and thus affecting the measured potential. To overcome this difficulty many of the solutions were ultrafiltered, with suction, through collodion membranes supported on sintered glass. This procedure yielded solutions which appeared optically clear in a Tyndall beam. Another procedure gave somewhat less complete, but apparently sufficient, removal of suspended material. This was the repeated filtration between each crystallization of the hot saturated solutions of potassium iodide, using the most dense hardened filter paper obtainable. The paper was pre-washed and supported on a steam-heated funnel. Solutions made up from this salt were very nearly optically clear and were used for part of the work. In earlier work the results appeared to be influenced by the presence of oxygen in the solutions, and elaborate precautions were made to exclude it from the solutions and the surroundings of the cell. With the use of ultrafiltration, the need of these precautions apparently disappeared. It seems possible that a really clean surface of platinum can overcome the disturbing effect of a small concentration of oxygen, whereas a contaminated surface is unable to do so. However, we do not consider the matter to be fully settled.

## The Experimental Results

**The Effects of Temperature Control.**—As mentioned above, correct, constant values of the e. m. f. of the galvanic cell were obtained only when there was no difference of temperature between the radii of the rotor corresponding to the positions of the electrodes $E_1$ and $E_2$. This is clearly indicated by some typical measurements illustrated in Fig. 3. In this figure the top curve shows the potentials of the galvanic cell, the next lower one the temperature of the rotor, and the bottom curve the difference of temperature at the points occupied by the electrodes, all plotted as functions of the time, the zero being the moment at which the rotor attained a speed of 5400 r. p. m. It will be seen that there is a quick rise of the e. m. f. of the cell, followed by a slower decrease. During the same period there is a slow increase of the temperature of the rotor, and a corresponding rise to a low maximum of the differential temperature. At a time indicated by the vertical dotted line running water was used to fix, at an appropriate point, the temperature of the rotor bearing. It will be observed in the figure that the differential temperature dropped rapidly to nearly zero, and shortly after the e. m. f. of the

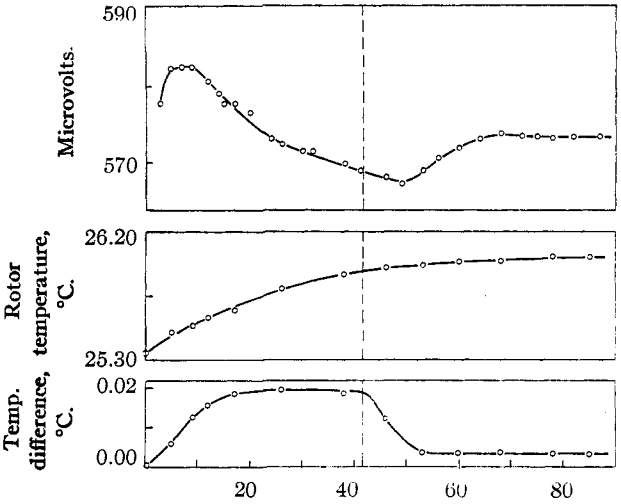

Fig. 3.—Effect of temperature difference on e. m. f. of cell and on rotor temperature.

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(7) MacInnes, *Rev. Sci. Inst.*, **14**, 14 (1943).

(8) Richards and Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

cell, and the temperature of the rotor, assumed constant values.

With experience, it was possible to adjust the temperature of the bearing at the start so as to avoid appreciable temperature gradients in the cell during the measurements. The measured potentials of the cell at each speed were, in general, established immediately, and remained constant, within one or two microvolts, for the period of the measurement, generally about ten minutes.

**A Typical Experiment.**—The results of a typical experiment are shown in line A of Fig. 4, in which the values of the potentials $E$, in microvolts, are plotted as functions of the square, $n^2$ of the speed of rotation in seconds. According to eq. 1 and the following eq. 8 this relation should be linear and pass through the origin. That A is a straight line is shown by plotting the slopes, $E/n^2$, against $n^2$ as shown in line B. The slope is thus seen to be constant within a very small limit of error. These data were obtained using solution 8, of Table I, in the galvanic cell.

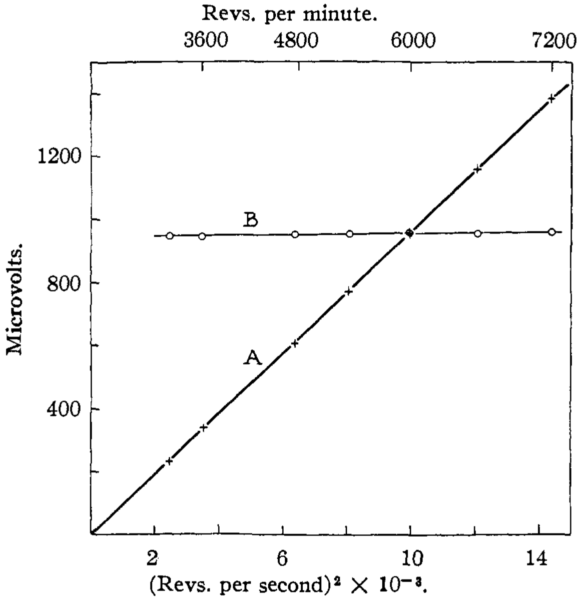

Fig. 4.—Results of a typical experiment.

Table I

Results of Measurements of Potassium Iodide–Iodine Solutions

| | Iodine normality | Density 25° | Molar cond. $\Lambda m$ 25° | $E/n^2$ × $10^8$ obs. | No. runs | Av. dev., % | $E/n^2$ × $10^8$ comp. |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 1.02037 | 126.70 | (6.71) | | | $6.68_4$ |
| 2 | 0.00165 | 1.02053 | 126.57 | $6.73_8$ | 2 | 0.1 | $6.71_2$ |
| 3 | .00990 | 1.02135 | 125.91 | $6.87_4$ | 4 | .1 | $6.85_3$ |
| 4 | .01981 | 1.02230 | 125.09 | $6.96_7$ | 2 | .05 | $7.00_5$ |
| 5 | .03961 | 1.02418 | 123.49 | $7.38_0$ | 5 | .4 | $7.34_1$ |
| 6 | .07922 | 1.02798 | 120.31 | $8.04_9$ | 1 | | $8.04_7$ |
| 7 | .1188 | 1.03178 | 117.15 | $8.85_1$ | 4 | .6 | $8.79_0$ |
| 8 | .1585 | 1.03558 | 114.05 | $9.58_6$ | 1 | | $9.60_4$ |

If, at the higher speeds, the experiment is prolonged the measured potentials drop slowly. This is to be expected, since, under the influence of the centrifugal force, there is a tendency of the salt and of the iodine to drift in the direction of the outer electrode. In an ultracentrifuge at much higher speeds than those used in our experiments Pedersen[9] attained sedimentation equilibrium for a number of salts, such as cesium chloride and lithium iodate.

The e. m. f. data plotted in Fig. 4 and recorded in Table I were obtained using a series of increasing speeds. The same accuracy has not yet been obtained with decreasing speeds, a phenomenon for which we can give no explanation.

**A Summary of the Measurements.**—Table I contains the results of a series of measurements on solutions of potassium iodide containing 0.1941 mole per liter at 25° and in addition varying amounts of iodine. The normalities of the iodine, *i. e.*, gram atomic weights per liter, are shown in column 2 of the table. The densities of the solutions, given in column 3, were determined by a magnetic float method which will be described in a future publication from this Laboratory. In the fourth column are given the observed molar conductances, $\Lambda_m = 1000\kappa/0.1941$, in which $\kappa$ is the measured specific conductance. We are indebted to Dr. Theodore Shedlovsky for aid in making these measurements, which were made with the conductance bridge developed in this Laboratory, and in an oil thermostat regulating to 0.003°. The $E/n^2$ values given in column 5 were obtained by the method of least squares from the original data. Each "run" consisted of an experiment such as is shown in the results plotted in Fig. 4, with the potentials, $E$, measured at seven different speeds. For the cases in which more than one run was made, as indicated in column 6, the average deviation in per cent. is given in the following column.

## Discussion of the Results

It will be seen from the data in Table I that the value of the quantity $E/n^2$ increases quite rapidly as the proportion of iodine in solution ascends. In the following discussion it is shown, quantitatively, that the effect is due to the effect of an iodide–iodine complex on the mechanism of the cell.

During the passage of current through the cell

$$(\mathrm{Pt});\ \mathrm{I_2},\ \mathrm{KI},\ \mathrm{I_2};\ (\mathrm{Pt}) \qquad (A)$$

the electrochemical reaction

$$\mathrm{I}^- = \mathrm{I}^0 + \epsilon^- \qquad (2)$$

occurs at the anode and at the cathode. Here

$$\epsilon^- + \mathrm{I}^0 = \mathrm{I}^-$$

$\mathrm{I}^0$ represents iodine in an uncharged condition. It may be in the form of $\mathrm{I_2}$ or as a complex $\mathrm{I}^-_{j+1}$ with the iodine ion, in which $j$ is the number of equivalents of uncharged iodine in the complex. During the passage of one faraday $F$ through the cell, $t_{\mathrm{K}}$ equivalent of potassium ion constituent

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[9] K. O. Pedersen, *Z. physik. Chem.*, **A170**, 41 (1934).

will migrate from the region of the anode and appear at the cathode, $t$ representing a Hittorf transference number. The remainder of the current is transported in the reverse direction by $t_I$ equivalent of $I^-$ and $t_C$ equivalent of the complex ion. The net loss around the anode is $t_K$ equivalent of potassium ion and $(1 - t_I - t_C) = t_K$ equivalent of negatively charged ion. Thus there is a net loss of $t_K$ equivalent of potassium iodide from the region of the anode. Since reverse phenomena occur at the cathode, a transport of $t_K$ equivalent of the salt from one electrode to the other takes place. This is accompanied by the appearance of one equivalent of $I^0$ at the anode by the electrochemical reaction, eq. 2, and $jt_C$ equivalent of that material by transference.

The transport process per faraday for the galvanic cell A is therefore $t_K$ equivalent of potassium iodide from the anode to cathode and $(1 + jt_C)$ equivalents of $I^0$ in the reverse direction. If gradients of chemical potential $\Delta\mu$ exist in the cell the Gibbs free energy $\Delta Z$ of its reversible operation will be

$$-\Delta Z = EF = t_K\,\Delta\mu_K - (1 + jt_C)\,\Delta\mu_{I^0} \qquad (3)$$

Since the operation of the cell takes place in a centrifugal field the chemical potentials $\mu$ will be functions of the radius $r$ in addition to the usual variables which are temperature, pressure, $P$, and the mole fractions of the components of the solution.

Assuming constant temperature and uniform concentration of the solution in the cell we have

$$\frac{d\mu_i}{dr} = \left(\frac{\partial\mu_i}{\partial r}\right)_P + \left(\frac{\partial\mu_i}{\partial P}\right)_r\frac{dP}{dr} \qquad (4)$$

Now the change of $\mu_i$ with $r$ is given by

$$(\partial\mu_i/\partial r) = -M_i\phi \qquad (5)$$

in which $\phi$ is the centrifugal force per unit mass and $M_i$ is the molecular or atomic weight. The negative sign is due to the fact that the energy of a component is increased by movement toward the center of rotation. The differential Gibbs free energy $dZ$ of a solution is given by

$$dZ = -s\,dT + V\,dP + \mu_1\,dN_1 + \mu_2\,dN_2 \ldots \mu_i\,dN_i \qquad (6)$$

in which $N_1, N_2, \ldots, N_i$ represent the numbers of moles. Since $dZ$ is an exact differential the partial molal volume $\bar{V}_i$ can be obtained by the cross differentiation[10]

$$\partial\mu_i/\partial P = \partial V/\partial N_i = \bar{V}_i \qquad (7)$$

Substituting $dP/dr = \rho\phi$ and eqs. 5 and 7 into eq. 4 we obtain

$$-d\mu_i/dr = \phi(M_i - \bar{V}_i\rho) = 4\pi^2 n^2 r(M_i - \bar{V}_i\rho) \qquad (8)$$

since $\phi = 4\pi^2n^2r$, in which $n$ is the number of rotations per second. Using this expression in eq. 3 after integrating between radii $r_2$ and $r_1$ yields[11]

$$-EF = 2\pi^2n^2(r_2^2 - r_1^2) \times [t_K(M_{KI} - \bar{V}_{KI}\rho) - (1 + jt_C)(M_I - \bar{V}_I\rho)] \qquad (9)$$

It will be observed that this equation reduces to eq. 1, as the proportion of iodine, and thus the transference number $t_C$, decreases. Thus using eq. 1 and a limiting value of $E/n^2$ obtained by a short linear extrapolation from the data in Table I the transference number of the potassium ion in 0.1941 normal potassium iodide is found to be $t_K = 0.487_3$. This agrees closely with the value 0.4887 obtained by Longsworth[12] by the quite independent method of moving boundaries. In our computation values of the partial molecular and atomic volumes $\bar{V}_{KI}$, and $\bar{V}_I$ are necessary. Longsworth gives a formula, based on existing density data, from which $\bar{V}_{KI} = 46.34$ is obtained, and the value $\bar{V}_I = 30.31$ was computed from the density data in Table I. These quantities will be the subject of another contribution from this Laboratory.

With the aid of the conductance measurements, given in Table I, for potassium iodide solutions, with varying proportions of added iodine, a test of the validity of eq. 9 may be made. Assuming Kohlrausch's law of independent ion mobilities[13] the measured equivalent conductance $\Lambda_m$ is given by

$$\Lambda_m = \lambda_K + (1 - R/j)\lambda_I + (R/j)\lambda_C \qquad (10)$$

in which the $\lambda$ values are equivalent conductances of ion constituents; $R$ is the ratio $C_{I^0}/C_{KI}$, and $j$ is, once more, the number of equivalents of uncharged iodine carried by the complex. From this equation

$$\lambda_C = \lambda_I - (j/R)(\Lambda_{KI} - \Lambda_m) \qquad (11)$$

and also

$$t_K = \lambda_K/\Lambda_m \text{ and } t_C = R\lambda_C/j\Lambda_m \qquad (12)$$

since transference numbers are the proportion of the total current carried by a given ion constituent. Substituting these values in eq. 9 we have

$$-FE = 4\pi^2n^2(r_2^2 - r_1^2) \times \left[\frac{\lambda_K}{\Lambda_m}(M_{KI} - \bar{V}_{KI}\rho) - \left(1 + \frac{R\lambda_I - j(\Lambda_{KI} - \Lambda_m)}{\Lambda_m}\right)(M_1 - V_I\rho)\right] \qquad (13)$$

To test the validity of this equation in terms of our experimental results we must have, in addition to the data given in Table I, values of the ion conductances $\lambda_K$ and $\lambda_I$. With the aid of Longsworth's[12] value 0.4887 of $t_K$ for 0.2 $N$ potassium iodide and the value of $\Lambda_m$ for solution 1 of Table I, $\lambda_K = 61.92$ and $\lambda_I = 64.78$ are obtained.

On the assumption that for the complex $I^-_{j+1}$,

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[10] The thermodynamic function, $Z$, applicable to processes at constant temperature and pressure, is of service here since, although there is a gradient of pressure along the galvanic cell, the cell mechanism does not involve any alteration of this pressure distribution. Equations 6 and 7 are eqs. Nos. 92 and 272 of Gibbs' "Equilibrium of Heterogeneous Substances."

[11] This equation is equivalent to equation 83, for the effect of height, in the paper by Koenig and Grinnell, *J. Phys. Chem.*, **44**, 463 (1940).

[12] Longsworth, THIS JOURNAL, **57**, 1185 (1935).

[13] This law is only approximate at 0.2 $N$, but it is a sufficiently good assumption for computing the relatively small term $jt_C$ of eq. 9.

$j$ should be an integer, values of $E/n^2$ were computed for $j = 1$, 2 and 3, corresponding to ratios $R$ from the data in Table I. Those for $j = 2$ are given in that table in the eighth column, and are seen to agree closely with the quantities $E/n^2$ obtained experimentally. That the experimental results indicate the presence of the complex $I_3^-$, and are not in accord with $I_2^-$ or $I_4^-$ is shown graphically in Fig. 5 in which values $E/n^2$ for $j = 1$, 2 and 3 computed from eq. 13 are given as functions of the ratio $R (= C_{I^0}/C_{KI})$ as abscissas and the corresponding experimental values of $E/n^2$ from Table I are plotted as small circles. Here again the indication is clearly in close quantitative agreement with $j = 2$, or the complex ion $I_3^-$.

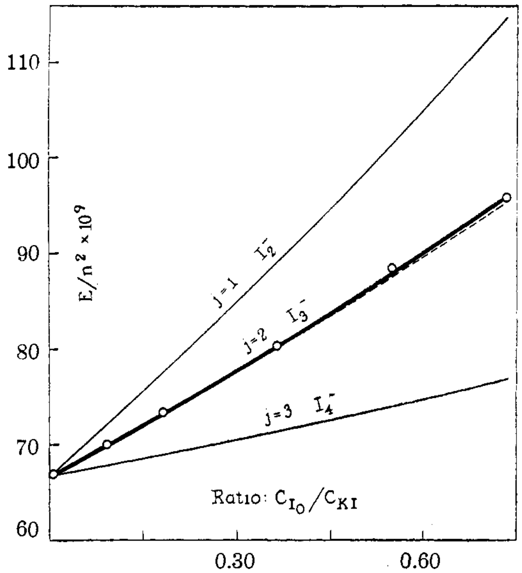

Fig. 5.—The variation of $E/n^2$ values with the ratio $C_{I^0}/C_{KI}$.

The existence of a complex of that composition has, from transference and distribution measurements, been known for a long time.[14] The results of this paper may, therefore, be regarded as a confirmation, by a quite new method, of the earlier conclusions.

A number of workers have determined the mass law constant for the equilibrium

$$I^- + I_2 = I_3^-$$

the most recent value being $1.40 \times 10^{-3}$ at 25° for a total iodide concentration of 0.2 $N$ as found by Jones and Kaplan.[14] A small proportion of the iodine in solution, therefore, exists in the form $I_2$ and the ratio $R$ should, strictly, be corrected for this effect. The effect of the correction is shown in Fig. 5 by the dotted line diverging from the curve for $j = 2$, and is within the experimental error of the present series of measurements.

## Summary

The potential, $E$, of a galvanic cell consisting of two iodide–iodine electrodes at two different radii in a rotor has been measured at different speeds of rotation, $n$. Reproducible potentials were obtained only when radial temperature gradients were eliminated and the solutions in the cell were free from suspended particles. A series of measurements were made on solutions which had a constant concentration of potassium iodide, but varying concentrations of iodine. For each solution values of $E/n^2$ were found to be accurately constant, through a range of values of of $n$ from 1800 to 7200 r. p. m. The ratio $E/n^2$ increases with the proportion of free iodine, a fact that is quantitatively accounted for by the presence in solution of the ionic complex $I_3^-$. The measurements also yielded a value of the transference numbers of potassium iodide in agreement with those obtained by the moving boundary method.

New York 21, N. Y. Received March 24, 1949

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[14] Bibliographies on the early work in this field are given by Bray and MacKay, This Journal, **32**, 914 (1910), and by Jones and Kaplan, *ibid.*, **50**, 1845 (1928).